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Trace-metal concentrations and mercury speciation in two soil profiles, Thunder Bay, Ontario

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Abstract: Southwest of Thunder Bay, Ontario, vertical geochemical soil profiles were examined to characterize the effects of soil-forming and weathering processes in pasture and woodland sites. Concentrations of Cu and Ni tend to increase with depth, whereas concentrations of Pb and Zn decrease. Profile comparisons indicate that deforestation and agricultural practice lead to loss of trace metals from soils. To determine if electrothermal vapourization and inductively coupled plasma mass spectrometry can distinguish different mercury forms and complexes in soils, samples from both profiles were analyzed. Preliminary results indicate that three Hg forms can be distinguished with concentrations that vary systematically through A, B, and C soil horizons. The most refractory Hg form occurs only in the A soil horizon of the pasture site. Electrothermal vapourization and inductively coupled plasma mass spectrometry has significant potential as an analytical tool for environmental studies.

Résumé : Au sud-ouest de Thunder Bay (Ontario), un examen de profils géochimiques des sols selon la verticale a été entrepris afin de caractériser les effets des processus pédogéniques et météoriques dans des sites de pâturage et de boisé. Les concentrations de Cu et de Ni tendent à augmenter avec la profondeur, alors que les teneurs en Pb et en Zn affichent un comportement inverse. La comparaison des profils indique que la déforestation et les pratiques agricoles ont entraîné une perte des métaux en traces des sols. Dans le but de déterminer si la méthode d'analyse par vaporisation électrothermique et spectrométrie de masse au plasma à couplage inductif permettait de distinguer les différents complexes et formes de mercure dans les sols, des échantillons des deux profils ont été analysés. Les résultats provisoires indiquent que trois formes de mercure peuvent être identifiées et que leurs concentrations varient de manière systématique à travers les horizons pédologiques A, B et C. La forme de Hg la plus réfractaire n'est présente que dans l'horizon pédologique A du site de pâturage. La méthode d'analyse par vaporisation électrothermique et spectrométrie de masse au plasma à couplage inductif révèle des possibilités intéressantes pour les études environnementales.

INTRODUCTION

As part of its Metals in the Environment (MITE) Program, the Geological Survey of Canada studies natural processes affecting soil geochemistry. Elements named on Environment Canada's Priorities Substances List, including copper, lead, zinc, and mercury, are the principal research focus. In large part, the biological and health risks represented by trace elements in the surficial environment depend on their chemical form, host (either inorganic mineral or organic compound), and concentration. Although partial extraction protocols can be used to characterize potential bioavailability (e.g. Hall et al., 1996), as a relatively volatile element, mercury is difficult to distinguish in inorganic mineral forms, including cinnabar, and in organic complexes.

Electrothermal vapourization and inductively coupled plasma mass spectrometry (ETV-ICP-MS) is an analytical approach that can potentially distinguish different mercury forms and complexes in soils, yielding information related to Hg bioavailability and the chemical processes transforming mercury. The use of stepwise thermal analyses for estimating mercury phases in soils is reported elsewhere (Azzaria and Aftabia, 1991; Windmöller et al., 1996; Biestert and Scholtz, 1997). Such analyses allow continuous detection of elemental and mercury compounds as they desorb and decompose. To test the potential for ETV-ICP-MS analysis to distinguish Hg forms, samples from two soil profiles near Thunder Bay, Ontario, were analyzed. The profiles were sampled as part of MITE research to characterize mercury in soils where concentrations are naturally elevated in underlying bedrock. The purpose of this report is to describe the geological and geochemical properties of the Thunder Bay soil profiles, and to present preliminary ETV-ICP-MS results in that context.

METHODS

In the northeastern corner of Scoble Township, 15 km southwest of Thunder Bay (lat. 48°17'17" N., long. 89°31'05" W), two soil profiles developed in fine-grained glacial lake sediments (Burwasser, 1977) were sampled. The profiles were about 20 m apart, one (98KY0033) in a pasture field and the other (98KY0034) in an adjacent woodland. The site is underlain by Hg-rich black shale of the Proterozoic Rove Formation, which also comprises argillite, shale, greywacke, and minor volcanic rock (Pye and Fenwick, 1965). The settlement and farming histories are unknown. The field site is currently used as cattle pasture whereas the woodland site is characterized by poplar trees with trunk diameters of ≥20 to 25 cm, indicating that it has likely not been cultivated for at least 30 years.

At each site, pits were dug to depths of ~150 cm using a backhoe, and soil profile samples were collected in 5 cm vertical increments. The sample increments were contiguous to depths of 60 cm; at greater depths, they are more widely spaced at 10 to 15 cm intervals. Textural analyses of bulk samples were done using a Lecotrac particle-size analyzer. For geochemical analyses, soil samples were air dried (30°C), and dry sieved to <0.063 mm using stainless steel sieves. The samples were analyzed using aqua regia and hot (60°C) 0.25M hydroxylamine hydrochloride acid digestions followed by inductively coupled plasma emission spectrometry (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Analyses were completed by Chemex Analytical Services Ltd., Vancouver, British Columbia. Results include a wide range of major (e.g. Fe, Al, Mg, Ca), minor (e.g. Mn), and trace elements (e.g. Cu, Pb, Zn); this report, however, focuses on trace metals (Hg, Cu, Ni, Pb, Zn). Iron and manganese profiles are included to broadly characterize soil development. Total mercury analyses were completed in GSC laboratories using a Milestone Analyzer system based on the adsorption of mercury on gold with subsequent atomic absorption detection. The mineralogy of the clay-sized (<0.002 mm) fraction was determined using X-ray diffraction analyses of normal, heat-treated, and glycolated glass slide mounts; mineralogical interpretations are by J. Percival and R. Knight (GSC). Total carbon content was estimated by combustion at 1350°C, followed by infrared analyses of carbon dioxide using a Leco carbon analyzer. Determinations of pH are based on methods outlined by Sheldrick (1984).

An ETV-ICP-MS analytical approach volatilizes or decomposes different mercury compounds at different temperatures to release elemental mercury. For analysis, a solid sample is placed in a small graphite boat that is contained within a resistively heated graphite tube and slowly heated. As the sample is heated to 800°C over a period of two minutes, analyte vapour from the sample is transported to an argon plasma via a flow of argon of about $1 L \bullet min^{-1}$. Individual mercury signals (separated on the time scale) appearing at different temperatures correspond either to different forms of mercury or to mercury locked in different mineral phases. The direct analysis of solids that have undergone no previous preparation or alteration (other than drying) ensures that chemical transformations of mercury species prior to analysis are minimal.

Selected silt- and clay-sized (<0.063 mm) samples from both soil profiles were submitted for ETV-ICP-MS analysis. A Perkin-Elmer SCIEX Elan 6100DRC ICP mass spectrometer equipped with an HGA-600 MS electrothermal vapourizer was used. Pyrolytic graphite-coated tubes were used throughout. A PTFE tube 80 cm long with a 6 mm inside diameter was used to connect the HGA-600 MS to the plasma torch. Optimization of the plasma and mass spectrometer was accomplished using solution nebulization prior to switching to ETV mode. No further optimization of the ICP mass spectrometer was required with the exception of small ($\pm$ 50 $mL \bullet min^{-1}$) variations in the carrier airflow rate.

Approximately 1 mg, weighed on a microbalance, of solid sample was placed into a small (5 mm) graphite boat (Analytikjena AG, Jena, Germany). To ensure that the boats were Hg-free, they were heated to 1250°C prior to the analyses. Using a GSC-designed calibrated insertion device, the graphite boat was carefully placed into the graphite tube via a removable end widow. The end window was then replaced, the dosing hole of the graphite tube was sealed with a graphite

probe, and the heating sequence was begun. A maximum temperature of 800°C was reached over a heating period of 200 s. Most mercury compounds volatilize at a temperature under about 400°C, with elemental mercury typically vapourizing at about 100°C. Signals arising from S, C, Cl, and Hg could be monitored simultaneously to obtain information about elemental associations. Peak-hopping signal measurements were used with a dwell time of 50 ms/analyte.

For the trial phase of these experiments, samples from both profiles were chosen for ETV-ICP-MS analysis.

RESULTS

Parent materials are dark brown, brown, and dark reddish-brown silt to clayey silt containing minor sand and clay. In section, the sediments are massive to thin bedded, with contorted and disrupted bedding. The massive brown silt contains fragments of brown to reddish-brown clayey silt laminae. The clay-sized component becomes more abundant with depth, from < 5 to 15 weight per cent, and the sand-sized component decreases from 5 to <1 weight per cent (Fig. 1). Pebbles characterize the uppermost 15 cm of the field site. Their relative abundance (<5 weight per cent) in the upper 15 cm of the field site is attributed to recent erosion and surface transport by sheetwash, as opposed to facies variation in the deposit. In adjacent fields, >10 cm thick surface accumulations of black shale pebbles overlie the A horizon as a result of recent erosion and downslope transport. Because of the topographic setting, the field site is likely more affected than the woodland site.

Soil structures are blocky with silt coatings to depths of ~40 to 50 cm and plant roots extending to ~55 to 60 cm depth. On the basis of colouration, secondary iron characteristic of the B soil horizon extends to depths of about 45 cm. Both sites are well drained and the soils appear to be brunisolic.

Parent materials are predominantly derived from Proterozoic sedimentary bedrock of the Sibley Group, which outcrops east of Thunder Bay, and the Rove Formation. This interpretation is consistent with the well sorted, fine-grained character of the sediments, the presence of carbonate minerals derived from the Sibley Group, and the nearly complete absence of pebble-sized and larger clasts of igneous and metamorphic origin.

Clay-sized (<0.002 mm) minerals are predominately quartz (24–36%) and feldspar (40–42%), with lesser concentrations of amphibole (7–10 %), illite (11–15%), and vermiculite (6–16%). Quartz and feldspar concentrations are highest and illite and vermiculite concentrations are lowest in the uppermost part of the profile. Quartz and feldspar occur predominantly in the coarse silt- and fine sand-sized fraction, and phyllosilicate minerals in the clay-sized fraction.

Total carbon contents decrease with increasing depth, from 5 to 6 weight per cent in the 0 to 5 cm depth interval to <0.5 weight per cent at about 45 cm (Fig. 2). An increase to ~1.5 weight per cent in the lowermost sample at the woodland site is inferred to reflect inorganic carbonate minerals. At equivalent depths, total carbon concentrations are consistently higher at the field site than at the woodland site. Throughout each profile, pH values increase with increasing depth; the uppermost samples at the woodland site are more acidic than at the field site (4.5 vs. 5.5), whereas the

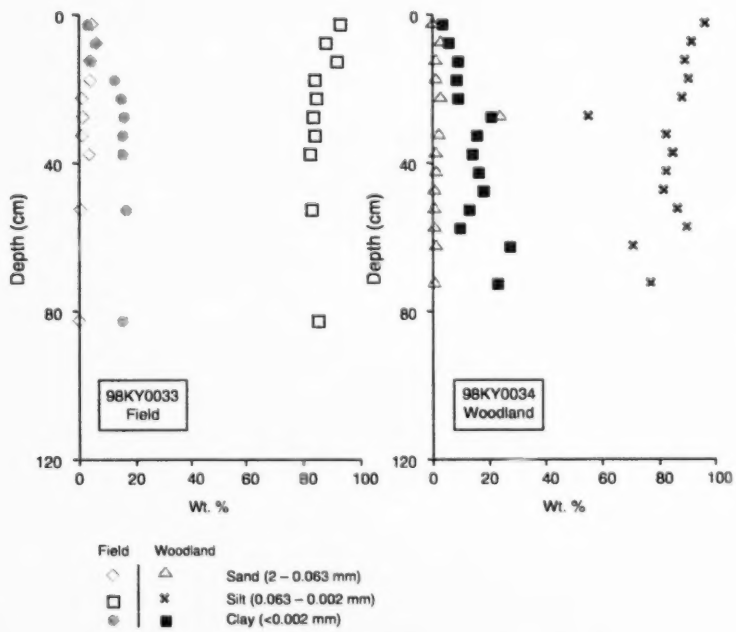

Figure 1.

Vertical textural profiles of sediments at the field (98KY0033) and woodland (98KY0034) sites.

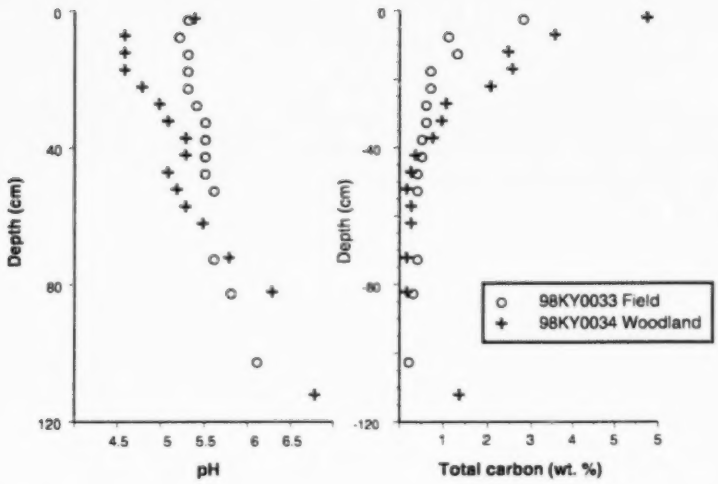

Figure 2.

Profiles of pH and total carbon at the field and woodland sites. The downward increase in pH reflects, in part, loss of carbonate minerals through reaction with soil organic acids. The upward increase in total carbon approximates the distribution of organic carbon.

lowermost samples are less acidic (6.8 vs. 6.2) (Fig. 2). At the woodland site, the pH profile shows a marked, localized inflection at about 45 cm depth.

The results of geochemical analyses indicate that concentrations determined after aqua regia digestion are consistently higher than those determined after hydroxylamine hydrochloride (Fig. 3). The two digestions show similar geochemical profiles. In both soil profiles, systematic geochemical changes with depth occur in the uppermost 50 cm; at greater depths, trends are either not evident or more weakly expressed. Depending on the element, vertical trends between profiles are either similar (e.g. Zn) or reversed (e.g. Mn, Hg). For example, with the exception of the uppermost sample, Mn and Hg concentrations increase downward to depths of about 50 cm at the field site (98KY0033), whereas they decrease downward at the woodland site (98KY0034). In both profiles, Cu concentrations increase downward whereas Pb and Zn concentrations decrease; for Ni there is no clear trend. For samples at equivalent depths in the upper 50 cm depth interval, trace-metal (Cu, Ni, Pb, Zn) concentrations are consistently lower at the field site than at the woodland site. At the field site, the uppermost sample (A soil horizon equivalent) can be enriched in some elements compared to the underlying B soil horizon. For instance, concentrations of Hg, Cu, Ni, and Mn are higher in the uppermost sample than in the underlying sample, which represents a reversal in the upward decrease shown in the profiles. In contrast, at the woodland site element concentrations are lower in the A equivalent horizon than in the underlying B equivalent horizon.

For each sample, ETV-ICP-MS Hg profiles comprise one to three distinct peaks distinguished by the time, in seconds, at which the signal peak is observed (Table 1). Among samples, the arrival times of the three peaks are similar, indicating that they represent three distinct Hg forms or associations. In this report the Hg forms associated with the peaks are referred to as Hg-1, Hg-2, and Hg-3, reflecting their arrival sequence.

INTERPRETATION AND DISCUSSION

Due to the proximity (<30 m) of the field and woodland sites, and to mixing and depositional processes associated with the glaciolacustrine environment, the silt-sized component of the parent materials is compositionally uniform within and between sites. Although reddish-brown and dark brown silt laminae indicate provenance variation, they are a minor component of what is otherwise massive brown silt. Hence, gross compositional differences within and between the vertical soil profiles are inferred to reflect predominantly the effects of postglacial weathering and soil formation, and differences between profiles are attributed to land use related to deforestation and agricultural practices. There has been loss of organic matter and elements (e.g. Hg, Fe, Mn, Cu, Ni, Pb, and Zn) from the upper part (<50 cm depth) of soil at the field site compared to the woodland site. Consistent with the known affinity of Pb and Zn for organic matter, concentrations of these elements increase upward through the B soil horizon along with carbon content. In contrast, Cu and to a lesser extent Ni have similar profiles at both sites, increasing in concentration with increasing depth, and both metals appear to be leached from the upper 0 to 50 cm depth interval.

The pH values in the upper part of the solum are higher at the field site than at the woodland site. In both profiles, the net downward increase in pH is inferred to reflect an increase in the proportions of calcium carbonate in the sediments. Carbonate minerals were likely present throughout the original deposits, and their relative absence in the upper 50 cm indicates that they were later removed through reaction with soil acids, preferentially so at the woodland site. Below 45 cm depth, Ca concentrations determined after aqua regia digestion (analyses results not shown) increase with increasing depth, consistent with this interpretation.

In the Thunder Bay area, soil parent materials derived from the Rove Formation are mercury-rich and contain hundreds to thousands of ppb Hg (unpub. MITE data, 1998, 1999, 2000). The concentrations in the two soils, however, are much lower (tens of ppb), which is consistent with a

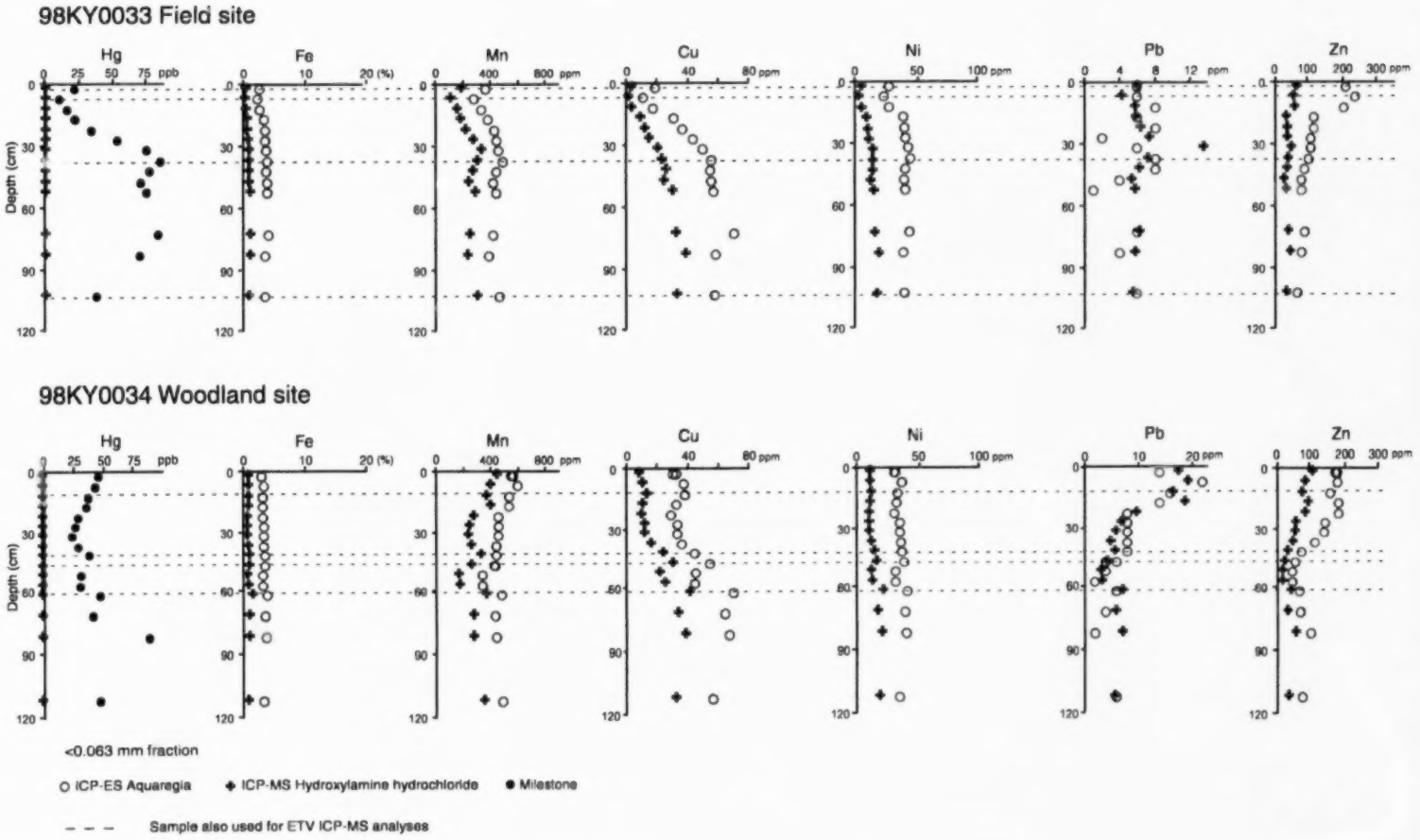

Figure 3. *Geochemical profiles of selected elements (Fe, Mn, Cu, Ni, Pb, Zn) determined after aqua regia and hydroxylamine hydrochloride digestions and Milestone (Hg) analyses. The geochemical trends differ among elements and between field and woodland sites.*

Table 1. Summary of soil properties and of peak arrival times and areas, expressed as a percentage, for ETV-ICP-MS Hg analyses.

	Sample No.	Average Depth (cm)	% Pebbles	% Sand	% Silt	% Clay	Munsell	pH	Total Carbon %	Peak1 ms	Peak 2 ms	Peak 3 ms	% Area 1	% Area 2	% Area 3
Field	98KY0033A	2.5	5.2	4.5	92.9	2.7	7.5YR3/2	5.3	2.8	47.8	68.7	135.5	6.0	36.5	56.5
	98KY0033B	7.5	1.1	6.3	88.0	5.6	5YR3/2	5.2	1.1	51.5	71.3	131.8	24.0	32.5	43.0
	98KY0033C	12.5	0.8	4.1	91.8	4.0	7.5YR3/2	5.3	1.3						
	98KY0033D	17.5	0.0	4.0	84.0	12.0	7.5YR4/2	5.3	0.7						
	98KY0033E	22.5	0.0	1.1	84.6	14.2	7.5YR4/2	5.3	0.7						
	98KY0033F	27.5	0.0	1.0	83.3	15.8	10YR4/3	5.4	0.6						
	98KY0033G	32.5	0.0	1.0	83.7	15.3	7.5YR3/2	5.5	0.6						
	98KY0033H	37.5	0.0	3.2	82.1	14.8	7.5YR4/2	5.5	0.5	51.9	60.4	0.0	41.5	58.5	0.0
	98KY0033I	42.5					10YR3/3	5.5	0.5						
	98KY0033J	47.5					10YR3/3	5.5	0.4						
	98KY0033K	52.5	0.1	0.7	83.0	16.2	5YR4/3	5.6	0.4						
	98KY0033L	72.5					7.5YR3/4	5.6	0.4						
	98KY0033M	82.5	0.0	0.0	85.1	14.9	7.5YR4/2	5.8	0.3						
	98KY0033N	102.5					10YR3/4	6.1	0.2	56.4	61.5	0.0	41.5	58.5	0.0
Woodland	98KY0034A	2.5	0.0	0.0	96.4	3.6	7.5YR3/2	5.4	5.8						
	98KY0034B	7.5	0.7	2.9	91.6	5.4	5YR2.5/2	4.6	3.6						
	98KY0034C	12.5	0.2	1.3	89.6	9.0	7.5YR3/2	4.6	2.5	53.2	68.0	0.0	23.5	76.0	0.0
	98KY0034D	17.5	0.2	1.3	90.5	8.3	5YR2.5/2	4.6	2.6						
	98KY0034E	22.5	1.1	2.9	88.4	8.7	7.5YR3/2	4.8	2.1						
	98KY0034F	27.5	21.1	23.7	55.6	20.7	7.5YR3/2	5	1.1						
	98KY0034G	32.5	0.1	2.2	82.6	15.3	7.5YR4/2	5.1	1						
	98KY0034H	37.5	0.2	0.8	85.2	14.0	7.5YR4/2	5.3	0.8						
	98KY0034I	42.5	0.6	1.2	82.7	16.1	7.5YR4/2	5.3	0.4	51.3	63.5	0.0	24.5	75.5	0.0
	98KY0034J	47.5	0.2	0.5	81.6	17.9	7.5YR4/2	5.1	0.3	46.7	63.2	0.0	35.0	65.0	0.0
	98KY0034K	52.5	0.0	0.6	86.4	13.0	7.5YR4/2	5.2	0.2						
	98KY0034L	57.5	0.0	0.7	90.0	9.3	7.5YR4/2	5.3	0.3						0.0
	98KY0034M	62.5	0.0	1.3	71.4	27.3	7.5YR4/2	5.5	0.3	53.3	66.9	0.0	47.5	52.0	
	98KY0034N	72.5	0.0	0.3	77.0	22.7	7.5YR3/2	5.8	0.2						
	98KY0034O	82.5					5YR3/2	6.3	0.2						
	98KY0034P	112.5						6.8	1.4						

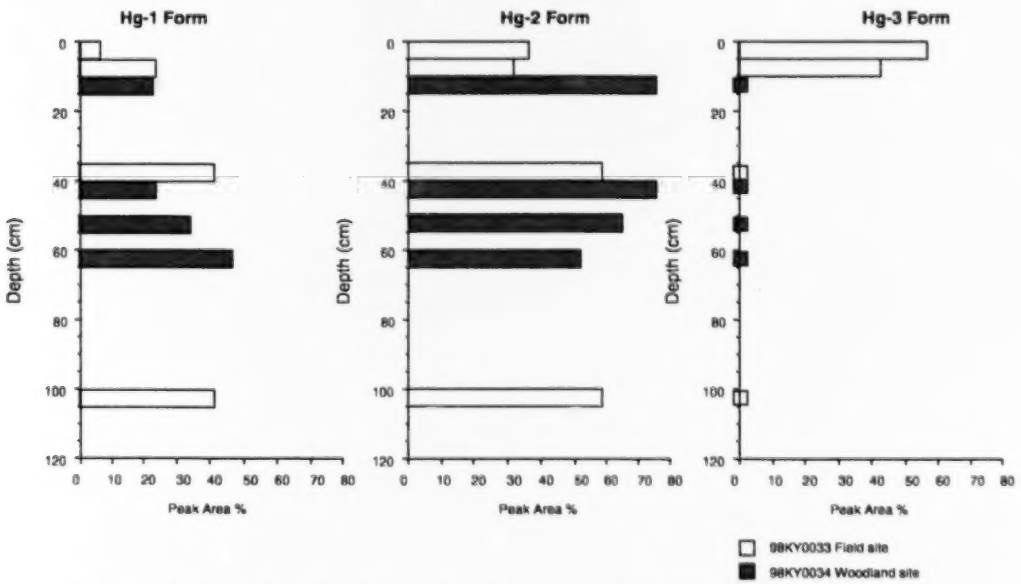

Figure 4. *Vertical profiles showing the relative concentrations of Hg-1, Hg-2, and Hg-3 forms in the field and woodland profiles. Samples of both profiles are combined on each profile, plotted according to depth interval. For the Hg-3 form, samples containing less than the detection limit are plotted as squares on the vertical axis.*

provenance dominated by Sibley Group bedrock. The Hg profiles differ from those of other trace elements. A comparison of the site profiles reveals that Hg has been removed from the upper 15 to 20 cm at the field site, and has accumulated in the underlying 20 to 70 cm depth interval (B and BC soil horizons). The apparent enrichment in the B and BC horizons at the field site contrasts with the woodland site where Hg concentrations decrease progressively with increasing depth to about 30 cm depth (B horizon). At depths greater than 30 cm, Hg concentrations are generally higher than in the upper B and A soil horizons, although differences between adjacent samples do not allow the identification of clear trends. The lowermost sample at the field site and samples at depths greater than 40 cm at the woodland site appear to reflect 'unweathered' background concentrations of about 30 ppb.

The ETV peak times indicate that Hg in the soil profiles has three distinct forms or associations; more refractory forms are associated with higher release temperatures and later peak arrival times. Elemental mercury, for example, would be the least refractory. The Hg-1 and Hg-2 forms occur throughout both profiles, whereas the Hg-3 form occurs only in the uppermost field site sample (Fig. 4). Using peak area as an indicator of relative abundance, the concentration of the Hg-1 form is lowest in the uppermost sample (0–5 cm) and increases downward to depths of ~40 to 50 cm, below which it does not change. Although ETV analyses are insufficient to define vertical trends in either soil profile, the following comments summarize apparent similarities and differences between them. Maximum concentrations of the Hg-1 form occur at greater depth (50–60 cm) at the woodland site than at the field site (20–40 cm). The Hg-2 concentrations are highest in the 15 to 50 cm depth interval and lowest in the 0 to 15 cm interval. Combining data from both profiles, Hg-2 forms appear to accumulate preferentially in the B-horizon. From ETV analysis, the most significant difference between sites is that the Hg-3 form occurs only in the 0 to 15 cm interval at the field site and was not found at the woodland site.

The composition and structure of the ETV Hg forms are unknown; studies are underway in our laboratories to determine which mercury species correspond to signals appearing at different times and temperatures. The vertical profiles indicate that different Hg species can reflect soil-forming and weathering processes. Differences between field and woodland sites indicate that the forms can be modified by land use. The Hg-2 form could represent an organic matter association characteristic of the B and BC horizons, with lower concentrations at the field site reflecting the breakdown and loss of organic matter resulting from deforestation and agricultural practice. The Hg-3 form, which occurs only in the uppermost sample at the field site, could be due to 1) an agricultural soil amendment, 2) a refractory Hg–organic matter association derived from biological processes associated with the field environment, or 3) input from an unknown source to the field site — possibly fine-grained black shale detritus carried in surface sheetwash.

CONCLUSIONS

From geochemical profiles, the effects of weathering and soil-forming processes are largely confined to the 0 to 45 cm depth interval — the A and B soil horizons. The effects can differ among trace elements, depending in part on their affinity for organic matter. Deforestation and land use can result in the loss of trace elements from the upper part of the soil profile (0–40 cm depth interval), in addition to loss of organic matter.

The ETV-ICP-MS data for Hg show promise as an analytical tool for differentiating different forms of Hg and their relative concentrations. Further studies to determine the nature of the ETV-ICP-MS mercury signal will likely make this analytical tool of great value for environmental studies.

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